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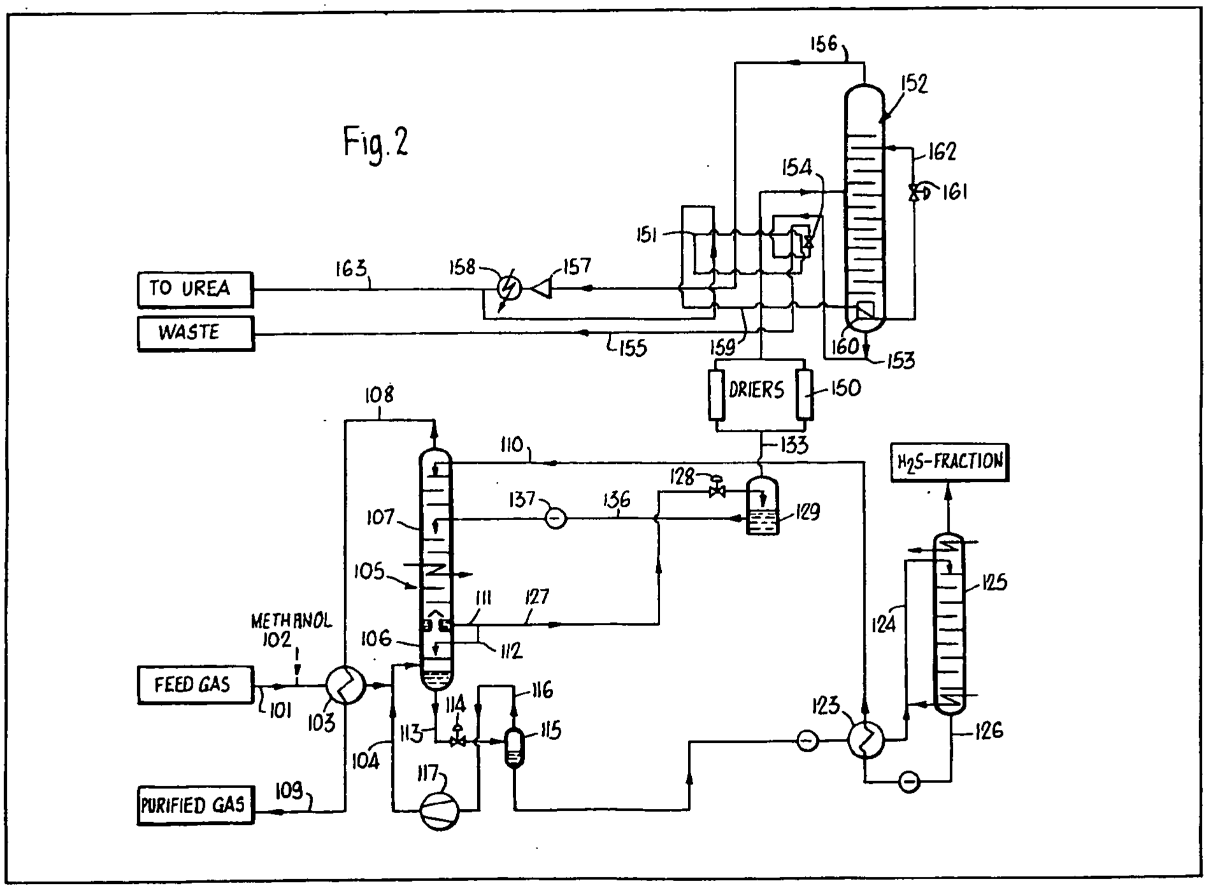
(54) Producing H_2 and CO_2 from partial oxidation gas

(57) H_2S, COS and CO_2 are removed from shifted partial oxidation gas by (1) physical absorption in a first stage 106 to remove the H_2S and some COS; (2) physical absorption in a second stage 107 to remove the CO_2 and the balance of the COS together with some H_2, CO and CH_4; (3) desorption 129 of the second stage solvent to recover the CO_2, COS, H_2, CO and CH_4; and (4) distillation 152 of the desorbed gases to recover the CO_2 free from COS. The distillation may be arranged to give a product stream comprising CO_2 together with H_2, CO and CH_4 or to give a product stream comprising CO_2 substantially free of H_2, CO and CH_4. The first stage solvent may be expanded 114 to release H_2 and CO_2 for recycle 104 and then regenerated to remove H_2S, COS and residual CO_2 in column 125.

Fig. 2



The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

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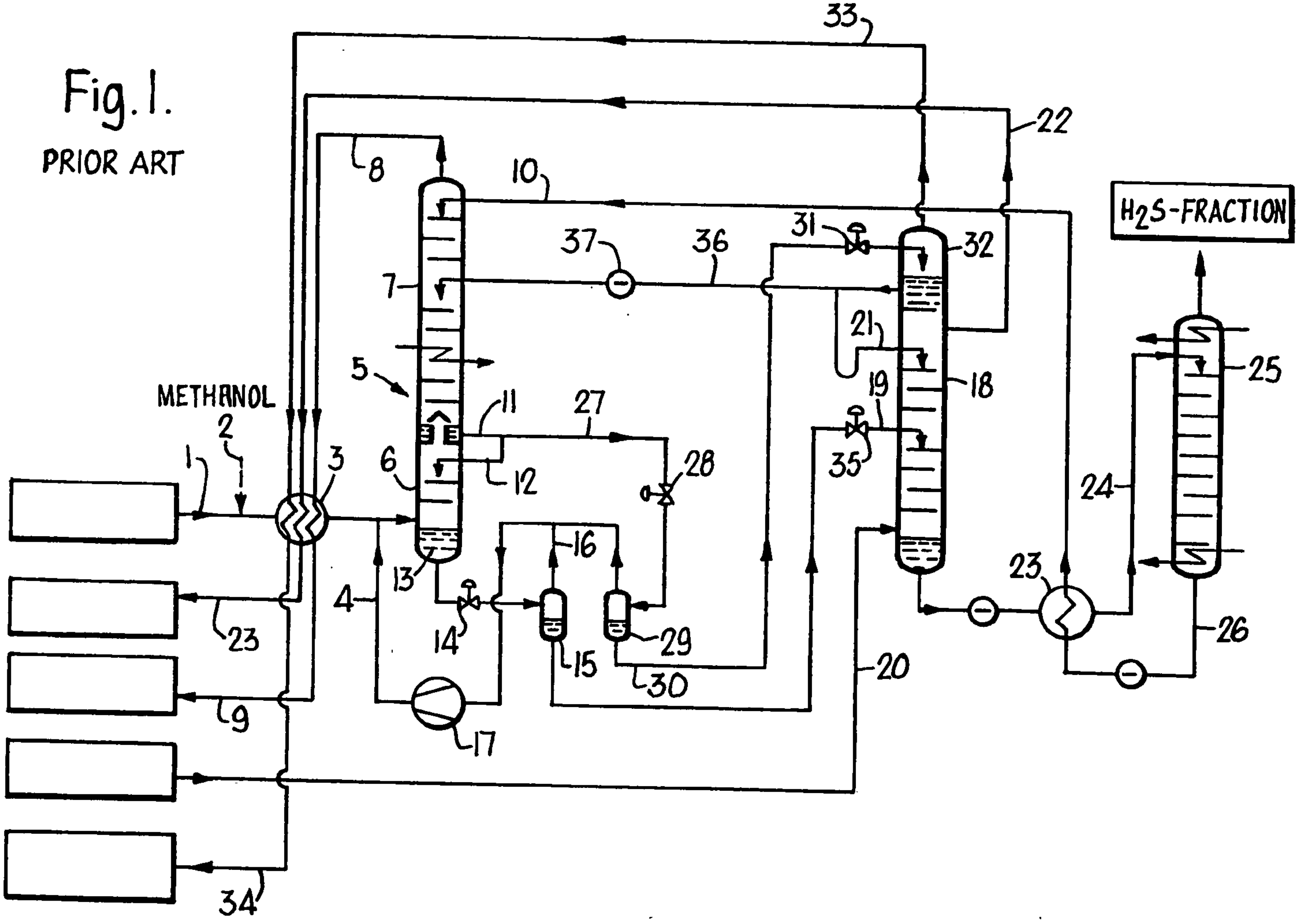
Fig.1.
PRIOR ART



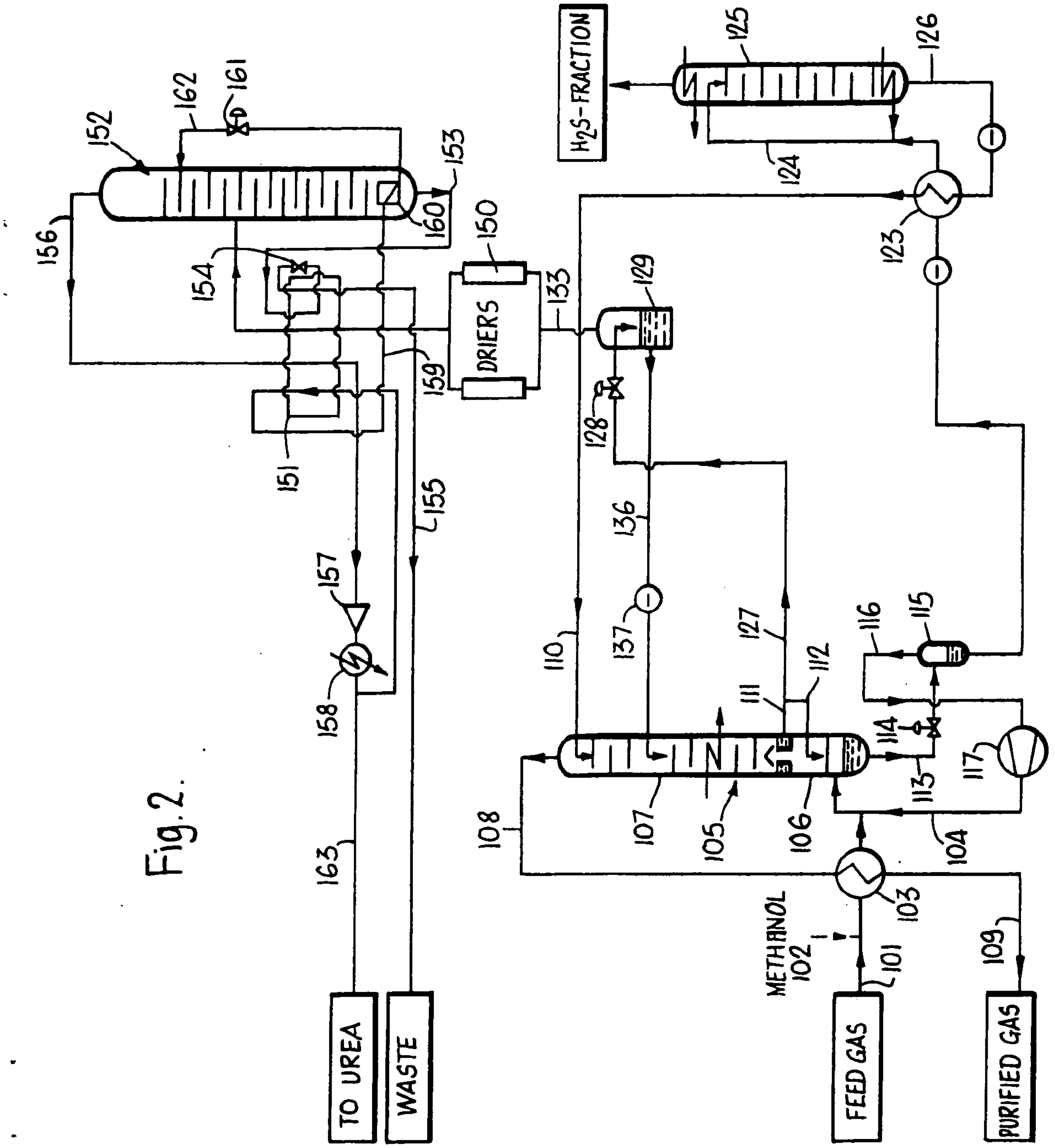

H2S-FRACTION
DRIERS
METHANOL
TO UREA
WASTE
FEED GAS
PURIFIED GAS

Fig. 2.

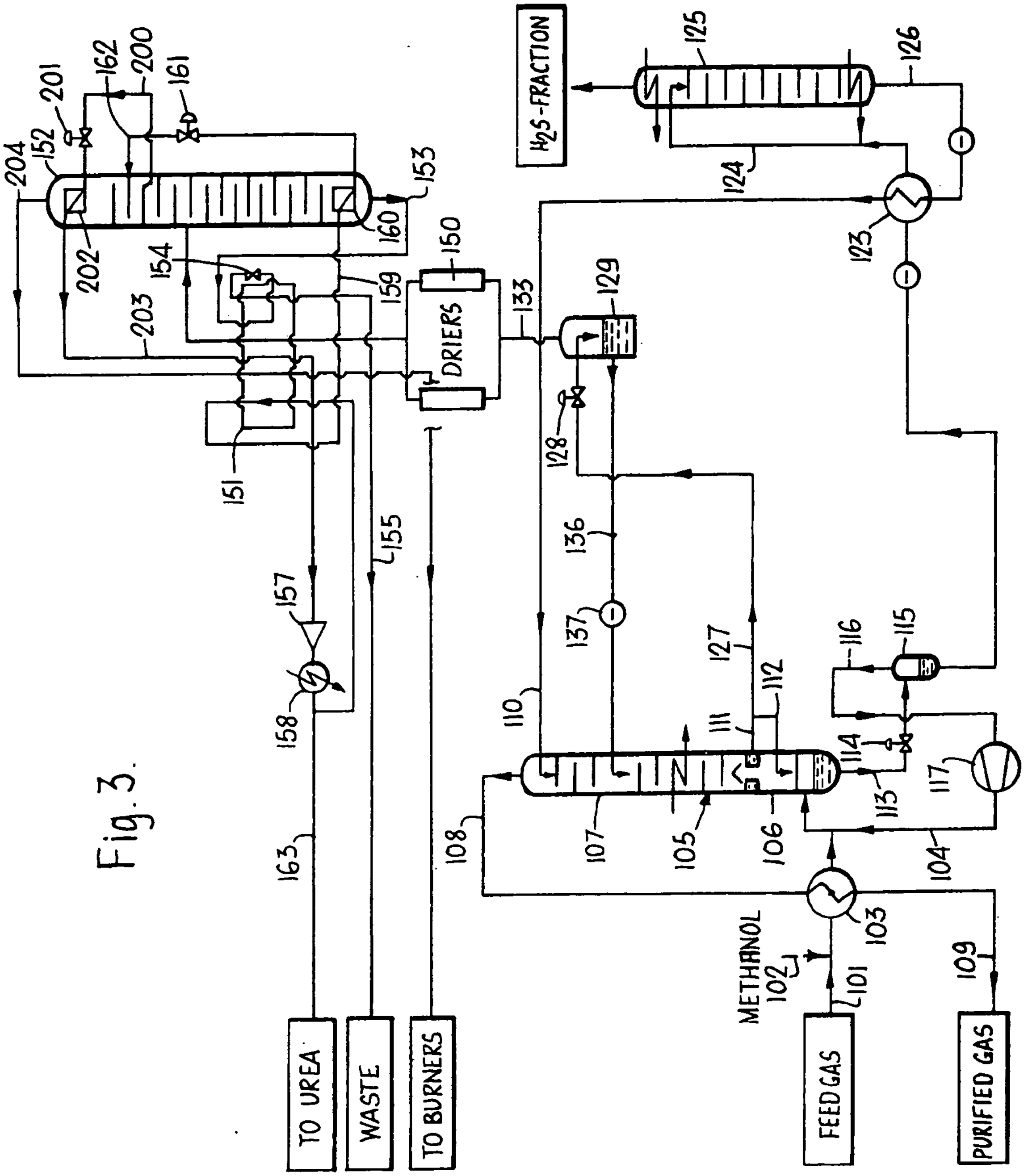

H2S-FRACTION
DRIERS
METHANOL
TO UREA
WASTE
TO BURNERS
FEED GAS
PURIFIED GAS

Fig. 3

SPECIFICATION

Method of treating partial oxidation gas to provide hydrogen for ammonia synthesis and CO_2 for urea

This invention relates to a method and an installation for treating a gas comprising H_2, CO_2, CO, CH_4, H_2S and COS to provide a stream of H_2 for an ammonia plant and a stream of CO_2 for a urea plant.

Commercially, urea is synthesized from ammonia and carbon dioxide. The urea synthesis plant is frequently situated immediately adjacent an ammonia synthesis plant since both the hydrogen for the ammonia synthesis and the carbon dioxide for the urea synthesis can be obtained from the same source, viz the gas obtained by the partial oxidation of oil or coal. Typically such gas, after being passed through a shift reactor, comprises (mole percent):

H_2	45 - 70%
CO_2	25 - 45%
CO	0.5 - 1.5%
CH_4	0.5 - 3%
H_2S	1.0 - 1.5%
COS	10 ppm - 0.5%
Ar/N_2	Balance

For the ammonia synthesis, the hydrogen must be recovered substantially free of all contaminants. In the case of CO_2 for urea plant feed, it is normal for a contactor to specify that the CO_2 must contain less than 1 ppm total sulphur. This is because any trace of hydrogen, carbon monoxide and methane must be oxidized before it enters the urea synthesis where it may form explosive mixtures with oxygen introduced to inhibit corrosion in the urea synthesis plant. Such oxidation is conventionally carried out over catalysts which are poisoned by even small amounts of sulphur.

Figure 1 is a flowsheet of an installation for obtaining CO_2 for urea synthesis plant. In particular, shifted partial oxidation gas enters the installation through line 1, typically at 33 bars A. Methanol is then added to the gas via pipe 2 and the mixture is cooled in heat exchanger 3. The mixture is then joined by a stream 4, and the combined stream is fed into the first absorption stage 6 of an absorption column 5 having a first absorption stage 6 and a second absorption stage 7.

Hydrogen containing small quantities of CO, CH_4, Ar and N_2 leaves the top of the absorption column 5 through conduit 8 and, after passing through heat exchanger 3, leaves the installation through conduit 9 en route to further purification before being passed to the ammonia synthesis plant.

Methanol enters the absorption column 5 through conduit 10. As it travels downwardly through the second absorption stage 7 it absorbs substantially all of the CO_2 present, together with some H_2, CO and CH_4. The saturated liquid is then withdrawn through conduit 11. Part of the saturated liquid is then passed through conduit 12 into the first absorption stage 6 where it absorbs all the H_2S and COS present. Because of the high flow rate of methanol necessary to absorb all of the COS, substantially quantities of CO_2 (almost 50% of that present in the initial feed) and H_2 are coabsorbed. The saturated liquid leaving the bottom of the absorption column 5 through line 13 is expanded at valve 14 to release most of the H_2 and some of the CO_2 absorbed. The two phase mixture thus formed is separated in phase separator 15 and the vapor phase is passed through line 16 to compressor 17 where it is recompressed before being recycled to the first absorption stage via conduit 4.

The H_2S/COS rich liquid, together with coabsorbed CO_2, from phase separator 15 is expanded at valve 35 and is then passed to column 18 through pipe 19. Nitrogen is introduced into the bottom of column 18 via conduit 20. The nitrogen strips out a substantial portion of the CO_2 remaining in the H_2S/COS rich liquid. At the same time, methanol containing some CO_2 is introduced into the top of column 18 via conduit 21 to reabsorb any H_2S and COS stripped by the nitrogen. The nitrogen and stripped CO_2 leave the column 18 through conduit 22 and leave the installation through conduit 23 after passing through heat exchanger 3. Normally, this stream contains too much total nitrogen and sulphur to be acceptable as urea plant feed.

The H_2S/COS rich liquid from the bottom of column 18 (which also contains some CO_2) is heated in heat exchanger 23 and passes through conduit 24 to regeneration column 25 where the H_2S and COs together with residual CO_2 are desorbed. Substantially pure methanol leaves the bottom of the regeneration column 25 through conduit 26, and after being cooled in heat exchanger 23, is recycled to the top of the absorption column 5 via conduit 10.

The balance of the CO_2 laden methanol in conduit 11 is passed through conduit 27 to valve 28 where it is expanded. The two phase mixture thus formed is separated in phase separator 29 and the gaseous phase comprising H_2 and some CO_2 is recycled to the inlet of compressor 17 as shown. The remaining liquid passes through conduit 30 to valve 31 where it is expanded and the two phase mixture thus formed is passed into two phase separator 32. CO_2 containing small quantities of H_2, CO and CH_4 essentially free of COS and H_2S leaves the separator 32 via conduit 33 en route to the urea synthesis plant via heat exchanger 3 and conduit 34.

Part of the methanol from separator 32, which still contains some CO_2, is returned to the absorption column 5 via conduit 36 and pump 37 whilst the balance is passed through conduit 21 as hereinbefore described.

Unlike H_2S, which is readily absorbed, COS is difficult to absorb and the flow of absorbent through the first absorption stage is determined by the requirement of absorbing all the COS. In addition, all such absorbent has to be heated before the absorbed H_2S and COS can be desorbed in regeneration column 25. These two factors combine to make desportion and pumping major factors in determining the operating cost of the installation.

We have discovered that a less energy consuming approach to this problem is provided by not attempting to remove all the COS in the first absorption stage. Instead, the residual COS and CO_2 and then absorbed (together with small amounts of H_2, CO and CH_4) in the second absorption stage. After desorption the remaining gas comprising CO_2 contaminated with COS, H_2, CO and CH_4 is distilled to provide a stream comprising CO_2 substantially free from COS and H_2S. If desired, the distillation may also be arranged to provide the CO_2 free from COS, CO, H_2 and CH_4 although freedom from the CO, H_2 and CH_4 is unnecessary bearing in mind that the urea synthesis plant is conventionally provided with a catalyst bed over which the H_2, CH_4 and CO can be oxidized in the presence of air or oxygen.

Once the need to remove all the COS in the first absorption stage is removed, the flow of absorbent through this stage can be reduced very substantially and not only does the pumping cost decrease, but simultaneously, the cost of heat for regeneration also decreased drastically. Against this must be set the energy costs of the distillation. However, such costs are considerably lower than the cost of the extra pumping and heating. These advantages are even more pronounced when using other physical solvents which have a lower affinity for COS relative to CO_2, for example ethers.

On the Investment side, adsorption column 5 and regeneration column 25 can be made smaller. Column 18 can be dispensed with although phase separator 32 must be maintained. The cost of absorbent is lower. However, against this a distillation unit must be provided. Calculations indicate that overall there should be a small saving in capital expenditure although this cannot always be guaranteed.

According to the present invention there is provided a method for treating a gas comprising H_2, CO_2, CH_4, H_2S and COS to provide a stream of H_2 for an ammonia plant and a stream of CO_2 for a urea plant, which method comprises the steps of scrubbing said gas with a physical absorbent to physically absorb substantially all of the H_2S and part only of the COS in the first absorption stage, absorbing the CO_2 and residual COs, together with some H_2, CO, CH_4 and residual H_2S (if any) in a second physical absorption stage, desorbing the CO_2, H_2, CO, CH_4, COS and H_2S (if any), and distilling the desorbed gas to provide a stream comprising CO_2 substantially free from COS and H_2S.

If desired, the distillation may be arranged so that the stream of CO_2 is also substantially free from H_2, CO and CH_4 although separation of the H, CO and CH_4 is unnecessary bearing in mind that these constituents are generally reacted with air or oxygen in a catalytically reactor immediately upstream of the urea synthesis reactor. In this connection the term "substantially free from H_2, CO and CH_4" means containing less than 200 ppm (by volume) flammibles (i.e. $H_2 + CO + CH_4$) and preferably not more than 100 ppm (by volume) thereof.

Preferably, the first absorption stage is arranged to remove all but 1 ppm H_2S and only that portion of the COS which is co-absorbed (typically 50% of the COS originally present). However, more COS, for example up to 70% of the COS originally present, can be absorbed in the first absorption stage if desired, although such absorption will involve increased absorbent pumping and regeneration costs.

The distilled stream of CO_2 should preferably contain less than 10 ppm total sulphur, and preferably less than 1 ppm total sulphur, and advantageously less than 0.5 ppm total sulphur.

The present invention also provides an installation for treating a gas comprising H_2, CO_2, CO, CH_4, H_2S and COS to provide a stream of H_2 for an ammonia plant and a stream of CO_2 for a urea plant, which installation comprises a first absorption stage for absorbing H_2S and part only of the COS from said gas by physical absorption, a second absorption stage for absorbing CO_2 and COS, together with some H_2, CO and CH_4 and residual H_2S (if any), means for desorbing said CO_2, COS, H_2, CO and CH_4, together with said residual H_2S (if any), and a distillation unit for separating said desorbed gas to provide a stream comprising CO_2 substantially free from COS and H_2S.

Preferably, the distillation unit comprises a distillation column and a conduit for withdrawing, in use, liquid rich in CO_2 from a location near the top of said distillation column.

For a better understanding of the present invention, reference will now be made, by way of example, to Figures 2 and 3 of the accompanying drawings, which are simplified flowsheets of two embodiments of an installation in accordance with the present invention.

Referring to Figure 2, shifted partial oxidation gas enters the installation through line 101, typically at 33 bars A. Methanol is then added to the gas via pipe 102 and the mixture is cooled in heat exchanger 103. The mixture is then joined by stream 104 and the combined stream is fed into the first absorption stage 106 of an absorption column 105 having a first absorption stage 106 and a second absorption stage 107.

Hydrogen containing small quantities of CO, CH_4, Ar and N_2 leaves the top of absorption column 105 through conduit 108 and, after passing through heat exchanger 103 leaves the installation through conduit 109 en route to further purification before being passed to the ammonia synthesis plant.

Methanol enters the absorption column 105 through conduit 110. As it travels downwardly through the second absorption stage 107 it absorbs substantially all the CO_2 present together with some H_2, CO and CH_4. It also absorbs the balance of the COS which is not absorbed in the first absorption stage 106. The balance of the COS is typically 10 to 50% of the COS in the feed gas and preferably 40% to 50% thereof. The saturated liquid is then withdrawn through conduit 111. Part of the saturated liquid is then passed through conduit 112 into the first absorption stage 106 where it absorbs all the H_2S but only part of the COS. Ideally only sufficient methanol passes through the first absorption stage to remove all the H_2S present and such COS as is coabsorbed. Because of the lower flow rate less CO_2 is coabsorbed in the first absorption stage 106 than in the installation described with reference to Figure 1 and hence regeneration can be simplified. In particular, the saturated liquid leaving the bottom of the absorption column 105 through line 113 is expanded at valve 114 to release most of the H_2 and CO_2 absorbed. The two phase mixture is separated in phase separator 115 and the vapour phase is passed through line 116 to compressor 117 where it is recompressed before being recycled to the first absorption stage 105 via conduit 104. The H_2S rich liquid, together with coabsorbed COS but little CO_2 is heated in heat exchanger 123 and passed through conduit 124 to regeneration column 125 where the H_2S and COs, together with residual CO_2 are desorbed. Substantially pure methanol leaves the bottom of regeneration column 125 125 through conduit 126, and after being cooled in heat exchanger 123 is recycled to the top of absorption column 105 via conduit 110.

The balance of the CO_2 laden methanol in conduit 116 is passed through conduit 127 to valve 128 where is is evaporated. The two phase mixture thus formed is separated in phase separator 129 and the liquid phase comprising methanol with some dissolved CO_2 and COS is returned to the second absorption stage 107 via conduit 136 and pump 137.

Vapour from the two phase separator 129 containing mainly CO_2 and COS together with H_2, CO and CH_4 passes through conduit 133 to one of a pair of guard driers 150 where any moisture present is removed. The dried gas is then precooled in heat exchanger 151 and introduced into distillation column 152 where it is separated into a gaseous product comprising CO_2, H_2, CO and CH_4 and a containing liquid entering the COS. The liquid leaves the distillation column through conduit 153 and is warmed in heat exchanger 152, expanded across valve 154, rewarmed in heat exchanger 151 and passed to waste through conduit 155. The overhead product leaves the distillation column 152 through conduit 156 and is heated in heat exchanger 151. The overhead product is then passed to the first stage 157 of the compressor train associated with the urea synthesis plant. After passing through aftercooler 158 part of the compressed overhead product is cooled in heat exchanger 151 and is then passed through conduit 159 to reboiler 160 where it is largely liquified. The liquid is then expanded at valve 161 and is introduced into the upper part of the distillation column 152 as reflux through conduit 162.

It should be noted that the product CO_2 in conduit 163 contains H_2, CO and CH_4 and that it is essential to incorporate a catalytic bed to remove these before they enter the urea plant. The need for such a catalytic bed can however be eliminated if the distillation unit described with reference to Figure 3 is used. In this connection it is believed the product of the unit described with reference to Figure 3 can be fed direct to a urea plant with little risk of an explosion although a small catalytic bed may be incorporated as a safety measure. Turning now to Figure 3 the same reference numerals as used in Figure 2 have been used where possible. The main difference is that instead of the CO_2 being withdrawn as a gaseous overhead product together with H_2, CO and CH_4 it is withdrawn as a liquid through conduit 200 situated near the top of the distillation column 152. Although the liquid contains some dissolved H_2, CO and CH_4 it is at a tolerable level, (i.e. below 200 ppm total flammibles). The liquid is let down across valve 201 and vapourized in reflux condensor 202. Vapourized liquid is then cooled in heat exchanger 151 before being passed through conduit 203 en route to the urea synthesis plant.

Reflux condenser 202 provides sufficient refrigerant so that the flow of gas through conduit 204 is relatively small and the gas contains mainly the flammibles, viz H_2, CO and CH_4 with a relatively small portion of CO_2. This gas is then passed through heat exchanger 151 and is burnt.

It should be appreciated that refrigeration for the distillation need not be obtained from the first stage 157 of the compressor train associated with the urea synthesis plants. Thus, refrigeration could be obtained from a separate closed cycle refrigeration unit.

The present invention is particularly advantageous when using physical absorbents having a relatively low affinity for COS compared with H_2S, for example ethers, n-methyl pyrollidone, propylene carbonate and tributylphosphate and still offers advantages for physical absorbents where this problem is less acute, for example methanol.

CLAIMS

1. A method for treating a gas comprising H_2, CO_2, CO, CH_4 and COS to provide a stream of H_2 for an ammonia plant a stream of CO_2 for a urea plant, which method comprises the steps of scrubbing said gas with an absorbent to physically absorb substantially all of the H_2S and part only of the COS in a first absorption stage, absorbing the CO_2 and residual COS together with some H_2, CO, CH_4 and residual H_2S (if

any) in a second physical absorption stage, desorbing the CO_2, H_2, CO, CH_4, COS and H_2S (if any) and distilling the desorbed gas to provide a stream comprising CO_2 substantially free from COS and H_2S.

2. A method according to Claim 1, wherein said distillation is arranged to provide a stream which is also substantially free from H_2, CO and CH_4.

3. An installation for treating a gas comprising H_2, CO_2, CH_4, H_2S and COS to provide a stream of H_2 for an ammonia plant and a stream of CO_2 for a urea plant, which installation comprises a first absorption stage for absorbing H_2S and part only of the COS from said gas by physical absorption, a second absorption stage for absorbing CO_2 and COs, together with some H_2, CO and CH_4 and residual H_2S (if any), means for desorbing said CO_2, COS, H_2, CO and CH_4, together with said residual H_2S (if any), and a distillation unit for separating said desorbed gas to provide a stream comprising CO_2 substantially free from COS and H_2S.

4. An installation as claimed in Claim 3 wherein said distillation unit comprises a distillation column and a conduit for withdrawing, in use, liquid rich in CO_2 from a location near the top of said distillation column.

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